Nano and Microspheres of Poly (aniline-formaldehyde): A Simple Synthesis

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Abstract

Nano and microspheres of novel poly (aniline-formaldehyde) [PANiFd] were synthesized through a simple mixing procedure using metal chlorides ($FeCl_3$+$AlCl_3$) under static condition.

Keywords

Nanosphere; Polyaniline; Spectral Studies; Chemical Synthesis

Introduction

Polymer nano and microspheres with intricate internal domain structures have been prepared from emulsion copolymerization [Chen et al. 1991] self-assembly of block copolymers [Zhang et al. 1997; Lu 2001; Li et al. 2004] and the sol-gel process [Lu et al. 1999]. Preparation of polymer nano and microspheres has been reported recently [Erhardt et al. 2001; Gohy et al. 2004; Hu et al. 2005; Zhang et al. 2005]. Polymer microspheres are not only pharmaceutically [Couvreur et al. 1997] important but also highly important for separation science (HPLC and SPE) [Wang et al. 2003] and in the catalysis field [Lu et al. 2001].

Aniline-formaldehyde resin is one of the most intensively investigated resin systems which is more utilized in the field of polyaniline (PANI) synthesis [Ho et al. 2005; Liu et al. 1997], sensor material [Misra et al. 2004; Dixit et al. 2005], matrix polymer for nano-composite preparation [Mathur et al. 1999; Vadera et al. 1997; Sharma et al. 2003) and metal removal from waste water (Kumar et al. 2006]. Based on the above background investigation on aniline-formaldehyde resin, the synthesis of nano and microspheres of poly (aniline-formaldehyde) has received much more attention. In this paper, we reported a simple and rapid one-step method to synthesize poly (aniline-formaldehyde) nanosphere (520nm) from aniline-formaldehyde resin using metal chlorides ($FeCl_3$-$AlCl_3$).

Experimental

Materials and Equipment

Aniline monomer was distilled under reduced pressure. Formaldehyde, 37% HCl, NaOH, $FeCl_3$ and $AlCl_3$ as well as other solvents were used as received. A morphological study of PANI was carried out using Hitachi 3000N (Japan) scanning electron microscope instrument operating at 10 kV. Fourier transform infrared spectra were recorded using GC-FTIR spectrometer (MODEL 670 Nicolet Nexus, USA). Wide angle X-ray diffraction spectra of powder samples were obtained using a Bruker/D8-Advance X-ray diffractometer using Cu, Kα radiation of wavelength 1.54 Å and continuous scan speed of 0.007°/min.

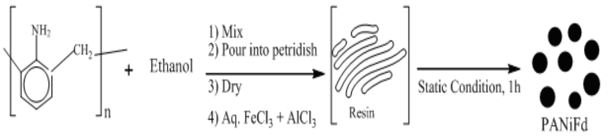
Synthesis

Aniline-formaldehyde resin was synthesized by reacting formaldehyde and aniline as described in the literature.[13] In a typical procedure, resin (1.0 g) was mixed with ethanol (20 mL) and transferred into petri dish, ethanol was evaporated at 50°C in an oven for 12 hrs; then 100 mL aqueous solution containing $FeCl_3$-$AlCl_3$ (9.6 g-0.4 g) was added into the petri dish, and the reaction was allowed to proceed under static conditions at ambient temperature. After 1 hr, the resultant brown precipitate of poly(aniline-formaldehyde) powder was filtered, washed with water (100 mL), followed by acetone (100 mL) and the sample was dried in an oven at 50°C for 4 hrs. Polymer samples were also prepared by changing the reaction time, reaction condition, amount of catalyst mixture and without solvent. PANiFd was not soluble in most of the organic solvents and no effort was made to determine the molecular weight of PANiFd.

Results and Discussion

Morphology of PANiFd Figure 1a-g shows the scanning electron microscopic picture (SEM) of PANiFd materials prepared under different reaction condition (Scheme 1). Nano and microspheres of PANiFd obtained in the present study are typically 520-1180 nm in size. The size of the sphere increases to

650, 790 and 800 nm with increases of reaction times to 1, 4 and 24 hrs respectively. In the 1 hr reaction time, the spheres are separated, and when the reaction time is increased to 4 hrs, the spheres merge with each other and then the particles separate again with 24 hrs of reaction time. The use of ethanol in the reaction plays an important role in the sphere formation; for example, the size of the sphere obtained is 790 and 1180 nm with the use of ethanol (Figure. 1b) and without using ethanol (Figure. 1d) respectively. Polymerization reaction carried out under constant stirring condition does not form sphere type and the particles are agglomerated with each other (Figure. 1e).



SCHEME 1 SYNTHESIS OF POLY (ANILINE-FORMALDEHYDE) [PANiFd] SPHERES

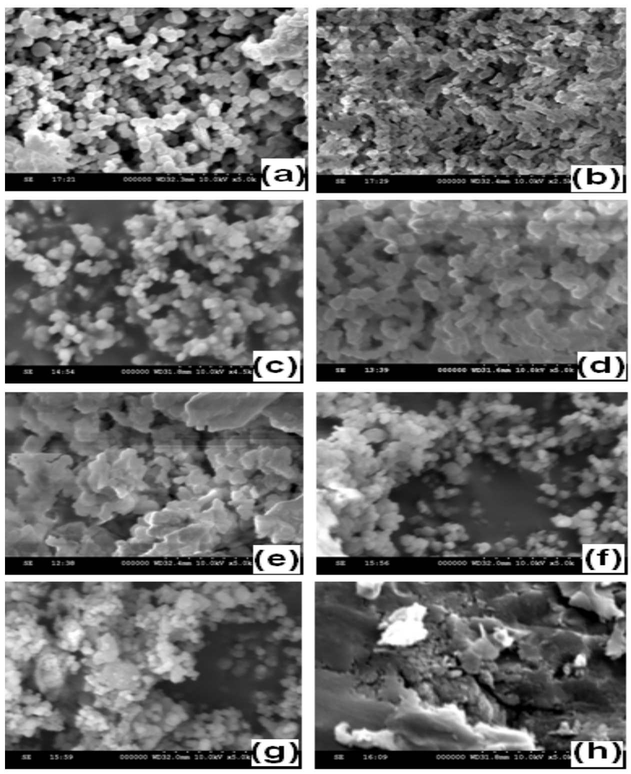


FIG. 1 SEM MICROGRAPHS OF (a) PANiFd SYNTHESIZED WITH EtOH-HEAT TREATMENT-1h; (b) 4h; (c) 24h; (d) PANiFd SYNTHESIZED WITH OUT EtOH-HEAT TREATMENT 4h; (e) PANiFd SYNTHESIZED UNDER STIRRING CONDITION-4h; (f) PANiFd SYNTHESIZED USING $FeCl_3 + AlCl_3$ (9.2g + 0.8g); (g) $FeCl_3 + AlCl_3$ (8.8g + 1.2g); AND (h) ANILINE POLYMERIZED IN PRESENCE OF $FeCl_3 + AlCl_3$ (9.2g + 0.8g)

Furthermore, the polymerization reaction was also carried out with various weight ratios of metal chlorides (9.6-0.4 g, 9.2-0.8 g and 8.8-1.2 g) with the size of the spheres of PANiFd decreasing to 660 (Figure. 1a), 650 (Figure. 1f) and 520 nm (Figure. 1g) respectively.

From the present results, it is difficult to understand why the different sizes of nano (micro) sphere are obtained with different ratios of $FeCl_3$-$AlCl_3$.

In order to find out the effect of -CH_2- linkage in the aniline-formaldehyde resin, we conducted the polymerization of aniline using $FeCl_3$-$AlCl_3$ under the same experimental condition. Since no sphere formation was observed (Figure. 1h), this result indicated that the -CH_2- linkage plays a main role in the PANiFd sphere formation.

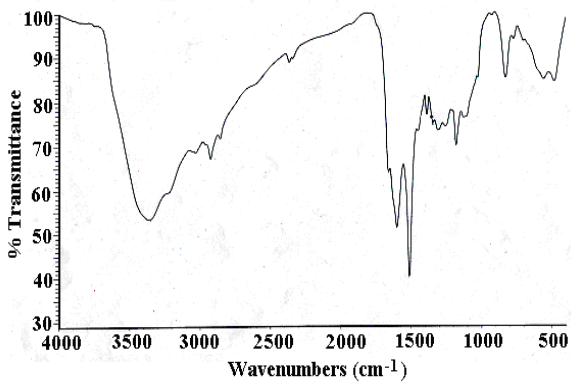


FIG. 2 FT-IR SPECTRA OF PANiFd SYNTHESIZED IN PRESENCE OF $FeCl_3$-$AlCl_3$

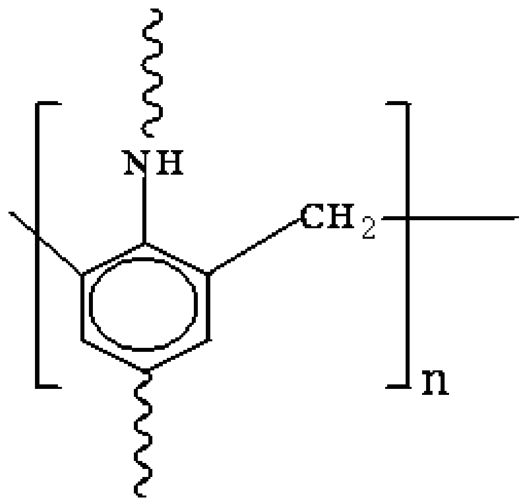


FIG. 3 STUCTURE OF PANiFd

FT-IR Study

The FT-IR spectrum of PANiFd is shown in Figure 2. A broad peak from 3355-3415 cm^{-1} is assigned to the N-H stretching vibration of PANiFd. The peak at 3,215 cm^{-1} is due to secondary N-H stretching. Peaks at 2,920 and 2,850 cm^{-1} are due to aliphatic C-H stretch, indicating the presence of formaldehyde-CH_2-moiety. Peak at 1,385 cm^{-1} is due to C-N aromatic stretching, confirming the presence of the amine moiety. The peak at 1,600 cm^{-1} is due to aromatic C=C ring

stretching, which also supports the probable structure of PANiFd as shown in Figure 3.

X-ray Diffraction Analysis

Figure 4 shows the X-ray diffractogram of polyaniline (Figure 4a), PANiFd materials synthesized using ethanol (Figure 4b) and without ethanol (Figure 4c). XRD patterns of all the three samples show peaks at 2θ = 33 and 36° corresponding to the interface distance d=2.69 and 2.515 A° respectively, indicating the presence of a Fe-Al complex in the polymer unit. The XRD patterns of PANiFd materials (Figures 4b, 4c) show broad peaks in the range 2θ=11-29°, indicating slight crystallinity compared to that of polyaniline (Figure 4a). XRD patterns of PANiFd materials synthesized with ethanol (Figure 4b) and without ethanol (Figure 4c) are found to be similar.

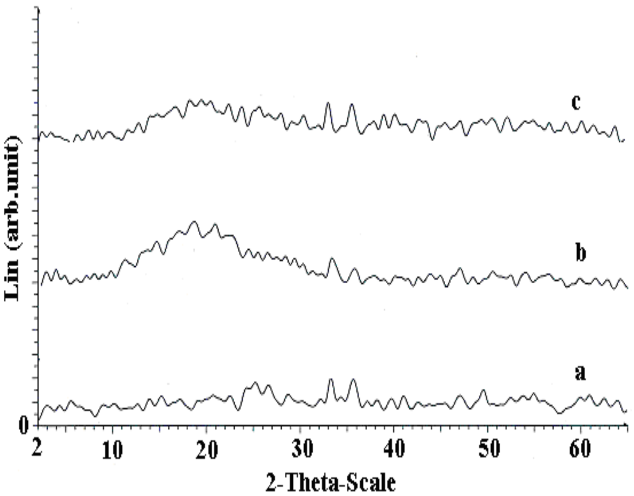


FIG. 4 X-RAY DIFFRACTOGRAM OF Fe–Al DOPED (a) POLYANILINE, (b) PANiFd SYNTHESIZED IN ETHANOL TREATMENT AND (c) PANiFd SYNTHESIZED WITHOUT ETHANOL TREATMENT

Conclusion

In summary, we have successfully demonstrated the synthesis of poly (aniline-formaldehyde) nano and microspheres from aniline-formaldehyde resin by a simple and facile method. While a complete understanding of this process remains elusive, the spheres produced may have many applications in such areas as pharmaceuticals and catalysis, etc. Further investigations concerning the chemical coupling of nano or microspheres with nanotubes to make superstructures and nanodevices are currently underway.

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His research work includes synthesis, characterization and evaluation of conducting polymer based materials for coating, batteries, supercapacitors, sensors, solar, polymeric light emitting diodes, electrostatic discharge materials, drug delivery and catalysts.